

Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA†

Cheryl A. Moody,^{a,‡} Gretchen N. Hebert,^b Steven H. Strauss^{*b} and Jennifer A. Field^{*c}

^aDepartment of Chemistry, Oregon State University, Corvallis, Oregon 97331, USA.

^bDepartment of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA.

E-mail: strauss@lamar.colostate.edu; Tel: (970)491-5104

^cDepartment of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon 97331, USA. E-mail: jennifer.field@orst.edu; Tel: (541)737-2265

Received 24th December 2002, Accepted 26th February 2003

First published as an Advance Article on the web 10th March 2003

Various formulations of fire-extinguishing materials, including aqueous film-forming foams (AFFFs), were used as part of fire-training exercises conducted at Wurtsmith Air Force Base (WAFB) in northeastern Michigan from the 1950s until the base was decommissioned in 1993. As a result of past fire-training exercises, AFFF-laden wastewater containing fuels, solvents, and other materials directly entered groundwater without prior treatment. Perfluorinated surfactants are key components in some AFFF formulations. In this study, groundwater was analyzed for perfluoroalkanesulfonates and perfluorocarboxylates. Perfluoroalkanesulfonates were directly detected using negative-ion electrospray ionization mass spectrometry. Derivatized perfluorocarboxylates were detected using electron impact gas chromatography-mass spectrometry. Groundwater from wells around fire-training area FTA-02 at WAFB contained four perfluorinated surfactants ranging in concentration from 3 to 120 $\mu\text{g L}^{-1}$: perfluorooctanesulfonate (PFOS); perfluorohexanesulfonate; perfluorooctanoate; and perfluorohexanoate. This is the first report demonstrating that PFOS, recently shown to be toxic to organisms ranging from zooplankton to primates, is still present in groundwater in measurable quantities five or more years after its last known use.

Introduction

Some perfluorinated surfactant anions, including perfluorooctanesulfonate, $\text{C}_8\text{F}_{17}\text{SO}_3^-$ (PFOS), have recently become pollutants of concern.^{1–11} Salts of PFOS are known to cause significant toxic effects, including mortality, in cynomolgus monkeys (oral doses of 0.75 $\text{mg kg}^{-1} \text{day}^{-1}$),¹² rabbits (oral doses of 3.75 $\text{mg kg}^{-1} \text{day}^{-1}$),¹³ rats (oral doses of 1.6 $\text{mg kg}^{-1} \text{day}^{-1}$),⁹ and zooplankton (exposure to 10 mg L^{-1}).¹⁴ Other biological effects of PFOS exposure have also been reported.^{1,15–23} The growing evidence that PFOS is toxic to higher organisms is noteworthy because it has been found in the tissues of many animals around the globe, including white rabbits in New Zealand, eagles near the Baltic Sea, various birds in Italy, Korea, Japan, and the southeastern US, polar bears in Alaska, river otters in Washington and Oregon, seals in the arctic regions of Canada and Norway, penguins in Antarctica, fish in the Pacific Ocean, Mediterranean Sea, and Lake Michigan, and oysters in the Gulf of Mexico and Chesapeake Bay.^{24–30} It is clear from this list that PFOS is distributed globally in the environment. Furthermore, PFOS concentrations up to 13 mg L^{-1} have been found in serum of fluorochemical plant employees in Alabama and Belgium.³¹ Additionally, 65 human serum samples obtained from four different US biological supply companies had PFOS concentrations ranging from 7 to 82 $\mu\text{g L}^{-1}$.³²

Salts of PFOS, or compounds that may degrade to PFOS, were used for years in many consumer and industrial formulations,

including fabric treatments, anti-static agents, paper coatings approved for food contact, shampoos, corrosion inhibitors, insecticides, and fire-fighting foams known as AFFFs (aqueous film-forming foams).^{1,2} AFFFs, some of which contain perfluoroalkanesulfonates³³ including PFOS,³⁴ have proven to be effective at extinguishing liquid-fuel fires and are widely and routinely used by civilian and US military fire-fighters.^{35–37} Historically, effluents from AFFF fire-fighting activities were neither impounded nor pre-treated prior to discharge to wastewater treatment systems or to the environment. Such releases may be responsible for the presence of PFOS in specific, localized environments. As far as the global distribution of PFOS is concerned, volatile perfluorooctanesulfonyl-containing compounds that may degrade to PFOS under environmental or biological conditions³⁸ were recently detected in ambient air in rural southern Ontario and in Toronto, ON.³⁹

The PFOS anion, like many other perfluorinated chemical species, is very stable.⁴⁰ It is resistant to thermal degradation and chemical attack in aqueous solution. For example, PFOS has been shown not to be metabolized by some pseudomonads,⁴¹ and its resistance to degradation in wastewater treatment systems causes excessive foaming that inhibits nitrification.⁴² Perfluorinated surfactants were detected in surface water downstream from an accidental spill site five months after the release.^{43,44} In addition, PFOS concentrations as high as 140 ng L^{-1} were detected in the Tennessee River 45 miles (72 km) downstream of a fluorochemical manufacturing facility in Decatur, AL (this value is significantly higher than the *ca.* 30 ng L^{-1} concentrations found upstream of the facility).⁴⁵ However, nothing has been published to date on the occurrence and persistence of perfluoroalkanesulfonates in the sub-surface environment. In this study, we report that PFOS and the related perfluorinated surfactants $\text{C}_6\text{F}_{13}\text{SO}_3^-$ (PFHxS), $\text{C}_5\text{F}_{11}\text{COO}^-$ (PFHxA), and

†Electronic supplementary information (ESI) available: Map of location of Wurtsmith Air Force Base, Oscoda, MI and surrounding states. See <http://www.rsc.org/suppdata/em/b2/b212497a/>

‡Current address: Lawrence Livermore National Laboratory, P.O. Box 808, Mail Stop L-232, Livermore, California 94551, USA

$C_7F_{15}COO^-$ (PFOA) are present at concentrations up to $120 \mu\text{g L}^{-1}$ in Michigan groundwater (1) up to 500 m from a site where AFFFs were routinely used for fire-fighting training activities and (2) at least five years after the cessation of fire-fighting activities.

Experimental section

Field site description and characterization

Wurtsmith Air Force Base (WAFB), which was decommissioned in 1993, is located in northeastern Michigan (see Fig. 1). Beginning in 1952, Fire-Training Area Two (FTA-02) at WAFB was used to train US military personnel in fire-fighting procedures. Training exercises consisted of flooding a concrete pad with flammable liquids, igniting the fluids, and extinguishing the fire with fire-fighting agents including AFFF.^{46,47} Although, the pad was the central location of recent fire-training activity, AFFF and other fire-extinguishing materials may have been used to extinguish fires in other areas at FTA-02.⁴⁸

The soil and groundwater at WAFB in the area around FTA-02 has been studied in detail.^{46–53} Benzene, toluene, ethylbenzene, and xylenes were found in the groundwater at concentrations ranging from 10 to $2,000 \mu\text{g L}^{-1}$.^{46,48} In this study, groundwaters from 68 wells at FTA-02 were tested for non-volatile total organic carbon (TOC) using a TOC analyzer (Model Dohrman DC-190, Rosemount Analytical, Santa Clara, CA). The TOC values ranged from 1 mg L^{-1} (detection limit) to 225 mg L^{-1} and confirmed previous findings that the groundwater in this area is contaminated with a variety of fuel-related contaminants.^{46–48} In addition to non-aqueous phase liquids,⁴⁹ a discontinuous 0.1 m thick layer of a black, tar-like substance occurs 0.3 to 0.9 m below the surface up to 50 m downgradient from the fire-training pad.⁴⁷ Groundwater from wells proposed to contain anionic surfactants from the use of AFFFs were tested for total anion concentrations using a standard method for methylene blue active substances.⁵⁴ Anion concentrations (calculated as PFOA, m/z 413) ranged from 400 to $10,200 \mu\text{g L}^{-1}$.

A contaminant plume at FTA-02 was previously defined in

several studies by examining groundwater from the numerous wells around the fire-training area for volatile organic compounds and specific conductance. The general plume boundary was approximated by specific conductance values greater than $250 \mu\text{S cm}^{-1}$.^{46–48} For this study, specific conductances (Purge Saver Model FC 2000, QED Environmental Systems, Inc., Ann Arbor, MI) of groundwater collected from 68 wells ranged from 110 to $3,170 \mu\text{S cm}^{-1}$, with the highest values measured near the fire-training pad area. The pH of the groundwater samples varied from 5.5 to 8.6.

Sample collection

Groundwater samples were collected from two types of monitoring wells at FTA-02 (Fig. 1). The position of the wells relative to the plume boundary are illustrated in Fig. 1 using the previously reported well designations.^{46–48,50–52} Monitoring wells with the identifier FT (fire-training) denote iron-cased 10 cm inner diameter wells with 1 to 2 m stainless steel screened intervals located 3 to 6 m below the water table.⁵² Wells with ML notations describe multilevel wells constructed from 2.5 cm inner diameter PVC casing with 0.3 m screened intervals that are vertically spaced from 0.5 to 2 m.⁵⁰ More detailed descriptions of these wells have been reported.^{46–48,50–52} Groundwater samples from ML3 and ML8 were collected in November 1998 and samples from the other wells were collected in June 1999. All samples were collected in high-density polypropylene bottles due to a report that perfluorinated carboxylates adsorb to glass.⁵⁵ It has since been shown that neither PFOS nor PFHxS adsorb to glass or to high-density polypropylene.³⁴ Samples were shipped on ice without preservation and stored at 4°C prior to analysis.

Standards and reagents

Potassium perfluorooctanesulfonate, K(PFOS), was synthesized from perfluorooctanesulfonyl fluoride (3M Company, St. Paul, MN) by adding potassium hydroxide in water and was recrystallized from water five times to a final purity of $>99\%$.³⁴ It was dried under vacuum at 25°C before use. Sodium dodecyl sulfate (DDS, Sigma, St. Louis, MO, 99%) was dried under vacuum at 25°C for 24 h and stored in a helium-filled glovebox. Perfluorooctanoic acid (98%), 2-chlorolepidine (99%; used as an internal standard), and iodomethane (used for perfluorocarboxylate methylations) were used as received from Aldrich (Milwaukee, WI).

Perfluoroalkanesulfonate and perfluorocarboxylate analyses

Quantitative perfluoroalkanesulfonate concentrations in the groundwater samples were determined using direct-injection negative-ion electrospray ionization mass spectrometry ((-)ES-MS) by the method of Hebert *et al.*³⁴ The sample preparation method included centrifugation to separate any fine particulates and dilution of each groundwater sample with acetonitrile to obtain solutions that were 1:1 (v:v) acetonitrile:water. These solutions were spiked with $133 \mu\text{g L}^{-1}$ DDS as an internal standard. Five replicate samples of each groundwater sample were analyzed. The concentrations of PFHxS in the samples were also determined using the DDS internal standard. This assumes that the (-)ES-MS sensitivity coefficients of PFOS and PFHxS are the same, a reasonable assumption since it is known that the sensitivity coefficients of PFOS and perfluorobutanesulfonate are the same.³⁴ Intensity ratios of PFOS (m/z = 499) and DDS (m/z = 265), $I(499)/I(265)$, were averaged and converted to PFOS concentrations using a calibration curve of $I(499)/I(265)$ ratio vs. PFOS concentration previously prepared using the purified K(PFOS) standard.³⁴ The calibration curve was linear over a range of PFOS concentrations from 5 to $2,500 \mu\text{g L}^{-1}$ (R^2 = 0.99). The detection limit (defined as a signal-to-noise ratio greater than 3)

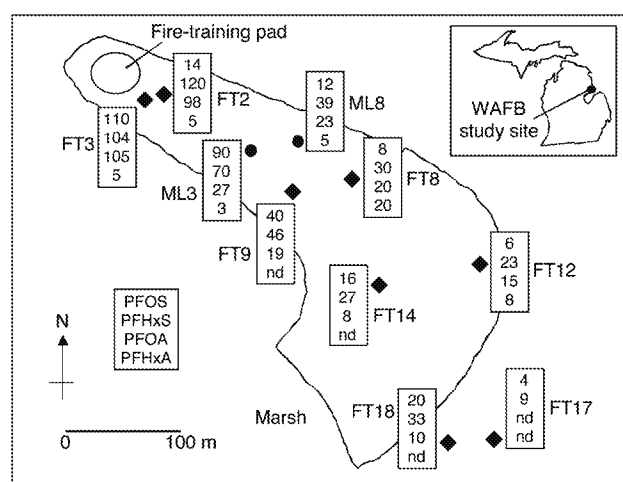


Fig. 1 Map showing the FTA-02 groundwater plume at retired Wurtsmith Air Force Base (WAFB), Oscoda, MI, USA. The inset shows the location of WAFB on a map of Michigan. (A larger area map showing surrounding states, south-central Canada, and the Great Lakes is available as Electronic Supplementary Information (ESI)†.) Groundwater samples from the indicated wells (diamonds and circles) were analyzed for perfluorooctanesulfonate (PFOS), perfluorohexanesulfonate (PFHxS), perfluorooctanoate (PFOA), and perfluorohexanoate (PFHxA). The boxes next to each well list the concentrations of the four analytes, in the order shown in the legend, in $\mu\text{g L}^{-1}$ (nd = not detected).

and quantification limit (defined as a signal-to-noise ratio greater than 10) for PFOS were 3 and 5 $\mu\text{g L}^{-1}$, respectively.

Perfluorocarboxylate concentrations were measured by the method of Moody and Field.⁵⁶ Strong anion exchange Empore disks were used to extract perfluorocarboxylates (6 to 8 carbons) from groundwater. The perfluorocarboxylates were simultaneously eluted from the disks and derivatized to their methyl esters by treatment with iodomethane for direct analysis by electron impact gas chromatography-mass spectrometry (GC-MS). A single analysis was conducted for each groundwater sample. The detection limit (defined as a signal-to-noise ratio greater than 3) and quantification limit (defined as a signal-to-noise ratio greater than 10) for perfluorocarboxylates were 3 and 13 $\mu\text{g L}^{-1}$, respectively, using 2-chlorolepidine as the internal standard. The concentrations of PFHxA and perfluoroheptanoate (PFHpA) in the samples were also determined using the 2-chlorolepidine internal standard, assuming a response factor equal to an equimolar amount of PFOA. Additionally, electron capture negative chemical ionization GC-MS was employed to confirm the identity of PFOA, PFHpA, and PFHxA in groundwater samples.

Results

Because one class of perfluorinated surfactants, perfluorocarboxylates, was detected in a limited number of groundwater samples from two other US military fire-training areas⁵⁶ as well as in commercial AFFF mixtures (unpublished data), the groundwater from FTA-02 was analyzed for these specific perfluorinated compounds as well as other perfluorinated surfactants found in commercial AFFFs. The concentrations of PFOS in WAFB groundwater from the wells shown in Fig. 1 ranged from 4 $\mu\text{g L}^{-1}$ to 110 $\mu\text{g L}^{-1}$ and the concentrations of PFHxS ranged from 9 $\mu\text{g L}^{-1}$ to 120 $\mu\text{g L}^{-1}$. Groundwater from all of the wells in Fig. 1 contained measurable concentrations of both PFOS and PFHxS. Relative errors in PFOS and PFHxS concentrations are listed in Table 1 and ranged from *ca.* 3% for the higher concentrations to *ca.* 50% near the detection limit. In addition to PFOS and PFHxS, some AFFF formulations contain relatively small amounts of at least three other perfluoroalkanesulfonate anions, perfluorobutanesulfonate, perfluoropentanesulfonate, and perfluoroheptanesulfonate.³⁴ However, these perfluoroalkanesulfonate homologues were not observed in any of the groundwater samples that were analyzed for this study.

The groundwater samples from FTA-02 had total perfluorocarboxylate concentrations ranging from the detection limit of 3 $\mu\text{g L}^{-1}$ to 110 $\mu\text{g L}^{-1}$, as shown in Table 1. Groundwater from half of the wells in Fig. 1 contained measurable concentrations of both PFOA and PFHxA. The PFHpA anion was observed in a few of the groundwater samples at the detection

limit (3 $\mu\text{g L}^{-1}$). Groundwater from a background well located at WAFB, but not at FTA-02, contained no detectable perfluorinated carboxylates (*i.e.*, <3 $\mu\text{g L}^{-1}$), indicating that the occurrence of perfluorocarboxylates in groundwater downgradient from the fire-training pad at FTA-02 are likely the result of AFFF applications and discharge during fire-training exercises. Of the three perfluorocarboxylate surfactants detected, PFOA was the dominant homologue, accounting for greater than 90% of the total mass of perfluorocarboxylates present. The observation of a suite of perfluorocarboxylates, as well as a suite of perfluoroalkanesulfonates, was expected since the raw materials used by the chemical industry to synthesize many perfluorinated organic compounds are mixtures.⁴⁰

Discussion

The highest concentrations of perfluoroalkanesulfonates and perfluorocarboxylates were observed in groundwater collected near the fire-training pad. Groundwater collected from wells located downgradient from the pad had lower concentrations. The data in Table 1 show that the total concentration of perfluoroalkanesulfonates was generally greater than the total concentration of perfluorocarboxylates. The ratios of total mass of perfluoroalkanesulfonates to total mass of perfluorocarboxylates varied from 0.95 to 5.4.

The presence of perfluoroalkanesulfonates in groundwater up to 500 m downgradient of the fire-training pad may indicate that this class of anionic surfactants migrates in the sub-surface environment. One important consideration for anionic perfluorinated surfactant transport is the organic content of soil. For example, Sullivan and Mabury determined that soil partition coefficients were linearly related to organic carbon content and sorption increased with increasing perfluorinated chain length.⁵⁷ More research will be required to fully investigate the factors that govern the transport behavior of perfluorinated surfactants.

The total concentrations of perfluorocarboxylates at WAFB FTA-02 were generally lower than previously observed in groundwater at Tyndall Air Force Base, FL and Naval Air Station Fallon, NV (124 to 298 $\mu\text{g L}^{-1}$ and 540 to 7,090 $\mu\text{g L}^{-1}$, respectively).⁵⁶ Groundwater samples were collected at these bases from wells around fire-training areas seven to ten years after cessation of fire-fighting activity. The frequency with which fire-training tests were conducted at the individual sites undoubtedly varied between sites and is only poorly documented. However, the presence of similar perfluorinated surfactants in the WAFB groundwater samples indicates the likely use of AFFFs of similar composition. Groundwater samples from Tyndall Air Force Base and Naval Air Station Fallon were not analyzed for perfluoroalkanesulfonates⁵⁶

Table 1 Concentrations of perfluoroalkanesulfonates and perfluorocarboxylates measured in the groundwater at FTA-02 at Wurtsmith Air Force Base

Well	Approximate distance from pad/m	PFOS/ $\mu\text{g L}^{-1a}$	PFHxS/ $\mu\text{g L}^{-1a}$	PFOA/ $\mu\text{g L}^{-1bc}$	PFHxA/ $\mu\text{g L}^{-1bc}$
FT2	17	14 \pm 2	120 \pm 20	98	5
FT3	18	110 \pm 10	104 \pm 3	105	5
ML3	114	90 \pm 8	70 \pm 10	27	3
ML8	121	12 \pm 2	39 \pm 4	23	5
FT8	183	8 \pm 2	30 \pm 10	20	20
FT9	183	40 \pm 10	46 \pm 8	19	nd
FT12	305	6.0 \pm 0.8	23 \pm 2	15	8
FT14	305	16 \pm 2	27 \pm 4	8	nd
FT18	518	20 \pm 10	33 \pm 4	10	nd
FT17	540	4.0 \pm 0.2	9 \pm 1	nd	nd

^aThe errors shown are ± 1 standard deviation and were calculated from five replicate analyses. ^bThe values listed are for a single analysis in each case. Based on past experience with this type of analysis,⁵⁶ the relative errors for these values probably range from 4% to 14%. ^cnd = not detected.

because a routine and reliable analytical method was unavailable at the time of analysis.

Recently, several reports of perfluorinated surfactants in surface waters have been published. Surface water collected from the Tennessee River near a fluorochemical manufacturing site contained concentrations of PFOS (17 to 144 ng L⁻¹) and PFOA (<25 to 598 ng L⁻¹) significantly lower than groundwater at WAFB FTA-02.⁴⁵ The observation of lower concentrations of perfluorinated surfactants in surface water is consistent with concentrations of PFOA (8 to 33 ng L⁻¹) found upstream of an accidental spill of fire-fighting foam into Etobicoke Creek, Toronto, ON.⁴⁴ The higher concentrations of PFOS (up to ~1000 µg L⁻¹) and PFOA (up to ~10 µg L⁻¹) found in the surface water downstream from the Ontario spill site are closer to the concentrations of perfluorinated surfactants found in the groundwater at WAFB FTA-02.

Conclusions

Despite a minimum of five years since active fire-fighting activity occurred at WAFB FTA-02, significant concentrations of perfluoroalkanesulfonates and perfluorocarboxylates were found in the groundwater. It is believed that the observed perfluorinated surfactants were components of some of the fire-fighting materials used at this site until 1993. The groundwater velocity is known to be 0.1 to 0.3 m day⁻¹ at this site.^{46,48,52} Assuming that the source of perfluorinated surfactants was the fire-training pad, we estimate that the perfluorinated surfactants found in groundwater *ca.* 500 m from the fire-training pad have been in the groundwater environment for a minimum of five years and potentially for as long as 15 years. The observation of perfluoroalkanesulfonates and perfluorocarboxylates in WAFB groundwater indicates that the compounds are resistant to degradation under the prevailing groundwater conditions at this site.

Acknowledgements

We thank M. J. Barcelona and S. K. Haack for facilitating sampling collection and technical assistance, and D. L. Dick, P. S. Craig, M. A. Odom, and B. J. Clapsaddle for experimental advice and assistance. We acknowledge Supelco, Inc. for the donation of vacuum manifolds and a GC column. This work was supported by the US NSF (grants CST-9726143 and CST-0085892 to Colorado State University) and by the US NIEHS (EHSC grant ES00210 to Oregon State University to support the Mass Spectrometry Core Facility).

References

- 1 US Environmental Protection Agency, *Fed. Regist.*, 2000, **65**, 62319.
- 2 US Environmental Protection Agency, *Fed. Regist.*, 2002, **67**, 11008.
- 3 D. Brown and C. E. Mayer, in *The Washington Post*, Washington DC, May 17, 2000, p. A1.
- 4 B. D. Key, R. D. Howell and C. S. Criddle, *Environ. Sci. Technol.*, 1997, **31**, 2445.
- 5 C. A. Moody and J. A. Field, *Environ. Sci. Technol.*, 2000, **34**, 3864.
- 6 R. Purdy, presented at the Society of Environmental Toxicology and Chemistry Conference, Nashville, TN, 2000, p. 160, abstract number PMP124.
- 7 R. Renner, *Environ. Sci. Technol.*, 2001, **35**, 154A.
- 8 R. Renner, *Sci. Am.*, March 17, 2001, p. 18.
- 9 A. Tullo, *Chem. Eng. News*, May 29, 2000, p. 12.
- 10 A. Tullo, *Chem. Eng. News*, May 22, 2000, p. 9.
- 11 A. Wood and W. Clarin, *Chem. Week*, May 24, 2000, p. 9.
- 12 A. M. Seacat, P. J. Thomford, K. J. Hansen, G. W. Olsen, M. T. Case and J. L. Butenhoff, *Toxicol. Sci.*, 2002, **68**, 249.
- 13 M. T. Case, R. G. York and M. S. Christian, *Int. J. Toxicol.*, 2001, **20**, 101.
- 14 H. Sanderson, T. M. Boudreau, S. A. Mabury, W.-J. Cheong and K. R. Solomon, *Environ. Toxicol. Chem.*, 2002, **21**, 1490.
- 15 J. Berthiaume and K. B. Wallace, *Toxicol. Lett.*, 2002, **129**, 23.
- 16 M. Derbel, M. Hosokawa and T. Satoh, *Biol. Pharm. Bull.*, 1996, **19**, 765.
- 17 T. Ikeda, K. Fukuda, I. Mori, M. Enomoto, T. Komai and T. Suga, in *Peroxisomes in Biology and Medicine*, ed. H. D. Fahimi and H. Sies, Springer-Verlag, Berlin, 1987, pp. 304–308.
- 18 A.-K. Sohlenius, A. M. Eriksson, C. Hogstrom, M. Kimland and J. W. DePierre, *Pharmacol. Toxicol.*, 1993, **72**, 90.
- 19 A. A. Starkov and K. B. Wallace, *Toxicol. Sci.*, 2002, **66**, 244.
- 20 D. J. Leubker, K. J. Hansen, N. M. Bass, J. L. Butenhoff and A. M. Seacat, *Toxicology*, 2002, **176**, 175.
- 21 B. Haugthom and O. Spydevold, *Biochim. Biophys. Acta*, 1992, **1128**, 65.
- 22 T. M. Boudreau, R. Janutka, K. R. Solomon, P. K. Sibley, D. C. G. Muir and S. A. Mabury, presented at the Society of Environmental Toxicology and Chemistry Conference, Nashville, TN, 2000, p. 77, abstract number 348.
- 23 T. M. Boudreau, R. Janutka, K. R. Solomon, P. K. Sibley, D. C. G. Muir and S. A. Mabury, presented at the Society of Environmental Toxicology and Chemistry Conference, Madrid, Spain, 2001, p. 129, abstract number M/MF144.
- 24 J. P. Giesy and K. Kannan, *Environ. Sci. Technol.*, 2001, **35**, 1339.
- 25 K. Kannan, J. Koistinen, K. Beckmen, T. Evans, J. F. Gorzelany, K. J. Hansen, P. D. Jones, E. Helle, M. Nyman and J. P. Giesy, *Environ. Sci. Technol.*, 2001, **35**, 1593.
- 26 K. Kannan, J. C. Franson, W. W. Bowerman, K. J. Hansen, P. D. Jones and J. P. Giesy, *Environ. Sci. Technol.*, 2001, **35**, 3065.
- 27 K. Kannan, K. J. Hansen, T. L. Wade and J. P. Giesy, *Arch. Environ. Contam. Toxicol.*, 2002, **42**, 313.
- 28 K. Kannan, S. Corsolini, J. Falandysz, G. Oehme, S. Focardi and J. P. Giesy, *Environ. Sci. Technol.*, 2002, **36**, 3210.
- 29 K. Kannan, J. Newsted, R. S. Halbrook and J. P. Giesy, *Environ. Sci. Technol.*, 2002, **36**, 2566.
- 30 K. Kannan, J.-W. Choi, N. Iseki, K. Senthilkumar, D. H. Kim, S. Masunaga and J. P. Giesy, *Chemosphere*, 2002, **49**, 225.
- 31 G. W. Olsen, J. M. Burris, J. H. Mandel and L. R. Zobel, *J. Occup. Environ. Med.*, 1999, **41**, 799.
- 32 K. J. Hansen, L. A. Clemen, M. E. Ellefson and H. O. Johnson, *Environ. Sci. Technol.*, 2001, **35**, 766.
- 33 *Material Safety Data Sheet for FC-203CF Light Water AFFF 3%*, 3M Company, Saint Paul, MN, 1999.
- 34 G. N. Hebert, M. A. Odom, P. S. Craig, D. L. Dick and S. H. Strauss, *J. Environ. Monit.*, 2002, **4**, 90.
- 35 R. D. Howell and E. E. Tucker, *Am. Environ. Lab.*, 1996, **12**, 10.
- 36 R. L. Darwin, R. E. Ottman, E. C. Norman, J. E. Gott and C. P. Hanauska, *Natl. Fire Protect. Assoc.*, 1995, 67.
- 37 D. B. Chan and E. S. K. Chian, *Environ. Prog.*, 1986, **5**, 104.
- 38 US Environmental Protection Agency, *Fluorochemical Use, Distribution and Release Overview*, 3M Company, 1999, pp. AR-226-0550.
- 39 J. W. Martin, D. C. G. Muir, C. A. Moody, D. A. Ellis, W. C. Kwan, K. R. Solomon and S. A. Mabury, *Anal. Chem.*, 2002, **74**, 584.
- 40 E. Kissa, *Fluorinated Surfactants: Synthesis, Properties and Applications*, Marcel Dekker, New York, 1994.
- 41 B. D. Key, R. D. Howell and C. S. Criddle, *Environ. Sci. Technol.*, 1998, **32**, 2283.
- 42 M. Erten-Unal, G. C. Schafran, S. Paranjape, E. Garcia-Cardona, H. Yan, F. Williams, D. Cotnoir, K. Clark and D. Kirk, *Proceedings of the 52nd Purdue Industrial Waste Conference*, 1998, **52**, 47.
- 43 C. A. Moody, W. C. Kwan, J. W. Martin, D. C. G. Muir and S. A. Mabury, *Anal. Chem.*, 2001, **73**, 2200.
- 44 C. A. Moody, J. W. Martin, W. C. Kwan, D. C. G. Muir and S. A. Mabury, *Environ. Sci. Technol.*, 2002, **36**, 545.
- 45 K. J. Hansen, H. O. Johnson, J. S. Eldridge, J. L. Butenhoff and L. A. Dick, *Environ. Sci. Technol.*, 2002, **36**, 1681.
- 46 *Phase II—Confirmation/Quantification Stage 1: Wurtsmith Air Force Base, MI: Investigations of Groundwater and Soil Contamination at Selected Sites*, United States Geological Survey, Lansing, MI, 1991.
- 47 *Phase II—Confirmation/Quantification Stage 2: Wurtsmith Air Force Base, MI, Investigation of Soil and Groundwater Contamination at Selected Sites, vol. I*, United States Geological Survey, Lansing, MI, 1995.
- 48 M. J. Barcelona, *Symposium on Natural Attenuation of Chlorinated Organics in Groundwater*, September 1996, p. 98.
- 49 J. L. Bermejo, W. A. Sauck and E. A. Atekwana, *Ground Water Monit. Rem.*, 1997, 131.

- 50 F. H. Chapelle, S. K. Haack, P. Adriaens, M. A. Henry and P. M. Bradley, *Environ. Sci. Technol.*, 1996, **30**, 3565.
- 51 M. A. Dojka, P. Hugenholtz, S. K. Haack and N. R. Pace, *Appl. Environ. Microbiol.*, 1998, **64**, 3869.
- 52 J. L. Gillespie, *Installation Restoration Program Phase II—Confirmation/Quantification Stage 2*, United States Geological Survey, Lansing, MI, 1990.
- 53 J. T. McGuire, D. T. Long, M. J. Klug, S. K. Haack and D. W. Hyndman, *Environ. Sci. Technol.*, 2002, **36**, 2693.
- 54 APHA-AWWA-WPCF, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington DC, 24th edn., 1998, ch. 5, pp. 47–49.
- 55 J. Belisle and D. F. Hagen, *Anal. Biochem.*, 1980, **101**, 369.
- 56 C. A. Moody and J. A. Field, *Environ. Sci. Technol.*, 1999, **33**, 2800.
- 57 R. C. Sullivan and S. A. Mabury, presented at the Society of Environmental Toxicology and Chemistry Conference, Baltimore, MD, 2001, p. 193, abstract number PM278.